Propane as a Thermodynamic Reference Fluid

NIST researchers have made new measurements of the heat capacity and pressure-density-temperature (p-ρ-T) properties of propane. These measurements, combined with carefully selected literature data, have been used to develop a new equation of state (EOS) of unprecedented accuracy. This new EOS will form the basis for future equations of state and other thermodynamic models developed at NIST.

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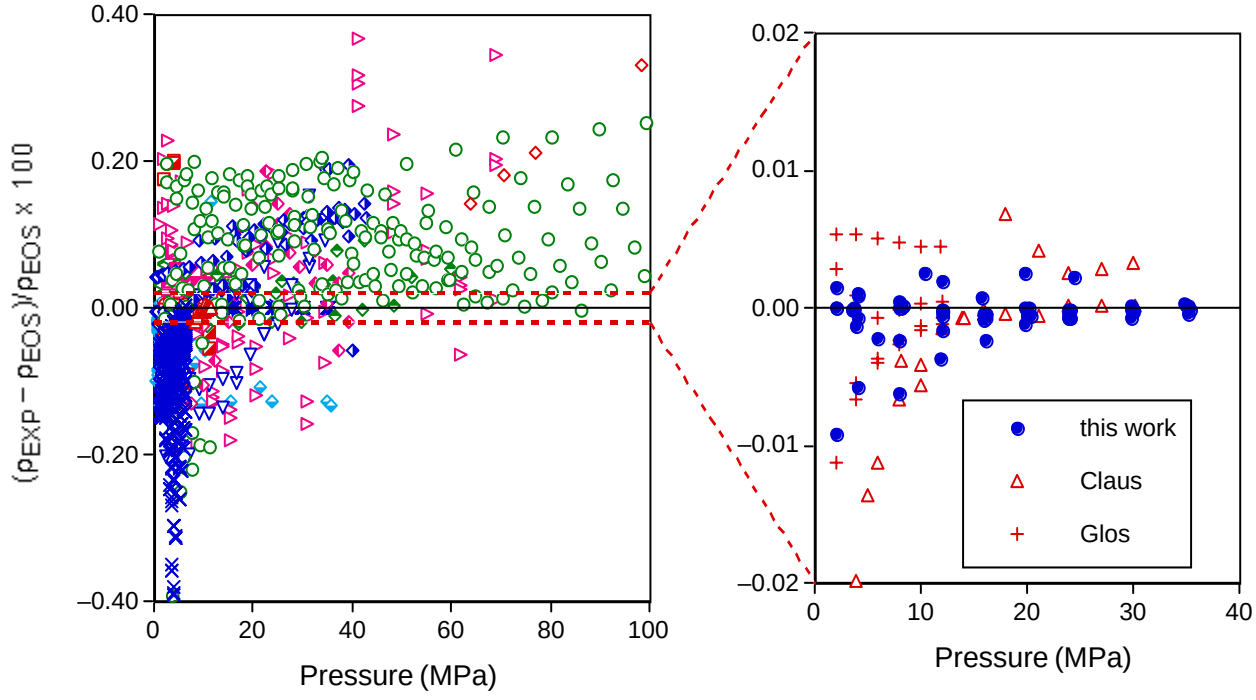
Propane C_3H_8 is an important industrial fluid, because it is not only a significant component of many natural gases but also a major fuel in its own right. But propane was selected for the present work because it is representative of the wide range of light hydrocarbons found in natural gas and liquid fuels. It is chemically stable and has an experimentally-accessible critical temperature of 369 K. It has the practical advantages of low toxicity, and commercial availability at very high purity. The ratio of its critical temperature to triple-point (freezing) temperature is among the highest of any fluid. These attributes make it an excellent reference fluid for the development of thermodynamic models.

Computerized databases, such as NIST REFPROP, employ equations of state – a mathematical representation of all the thermodynamic properties of a fluid. An EOS allows calculations at any condition and also provides values for properties, such as entropy, which cannot be measured directly. While some EOS are based on theory, the most accurate ones covering wide ranges of temperature and pressure are empirical and must be fitted to extensive experimental data.

The pressure-density-temperature (p-ρ-T) properties are the most essential data for fitting an EOS. In the current work, we have employed a new two-sinker densimeter to measure the (p-ρ-T) properties of high-purity (99.999 %) propane at temperatures from 265 K to 500 K with pressures to 36 MPa. The measurements extend from low-density vapor to compressed liquid states, and the near-critical region was covered extensively. The uncertainty (k = 2) in density is ±(0.0025 % + 0.0006 kg/m^3) at 293 K, increasing to ±(0.02 % + 0.001 kg/m^3) at 500 K.

The data shown here represent some of the most accurate data available for propane.

The figure shows the measured densities for compressed liquid propane compared to the new equation of state. Although numerous literature sources exist (each symbol represents a different source), most exhibit very large scatter and uncertainties; the new data (blue circles) have uncertainties that are a factor of 20 lower than most previous data, and they are in excellent agreement with two sets of recent, high-accuracy measurements.



Data for the heat capacity are also vital. While it is possible, in principle, to compute the heat capacity from an equation of state fitted only to (p-ρ-T) data, this involves the evaluation of multiple first and second derivatives; any small errors in the (p-ρ-T) data would be greatly magnified. We have measured the heat capacity at constant volume C_V, using the same propane sample, from the triple point temperature of 85.48 K to 345 K with pressures to 35 MPa. Measurements of the heat capacity at saturation C_{sat} were also used to determine the vapor pressure from 85 K to the boiling point at 231 K.

The equation of state is expressed in terms of the Helmholtz free energy as a function of the temperature and density. The Helmholtz free energy, A, is equal to U – TS, where U is the internal energy of the system, T is the absolute temperature, and S is the entropy. This equation is useful because calculation of all the other thermodynamic properties (including enthalpy, heat capacity, speed of sound, vapor pressure, etc.) require only the Helmholtz energy or its temperature or density derivatives. The general form of the equation is well established, but new terms were used to represent the liquid-vapor critical region. The new EOS has 20 terms, about one-half the number compared to other equations of comparable accuracy. Nonlinear fitting techniques were used, and this approach demands high quality data, otherwise it is possible to fit systematic errors in the data rather than the real fluid behavior. The new experimental data, combined with carefully selected literature data, were vital for obtaining a successful fit. The EOS not only fits the experimental data within its error, it also displays qualitatively correct extrapolation behavior down to 40 K in temperature and to extremely high temperatures and pressures. This was achieved by placing theoretically based constraints on the non-linear fit.

This new EOS will serve as a reference in several different ways. First, the functional form will serve as the starting point for the fitting of other high-accuracy EOS; it has already been applied in this way to the refrigerants R227ea and R365mfc. The new propane EOS will serve as the reference fluid in extended corresponding states (ECS) models. The corresponding states concept is based on the observation that broad classes of fluids have similar properties when scaled by the critical temperature and density; ECS models add an additional parameter, the shape factor, which is based on the molecular size and shape. The wide two-phase range of propane makes it an excellent choice for this application. ECS models are particularly useful for fluids with very limited data. Finally, the new EOS will be used to develop simplified equations of state for fluids with intermediate data—those with not enough data to develop a full high-accuracy EOS, but with more than the very limited data suited to an ECS model.

This work was presented in three talks at the 16th Symposium on Thermophysical Properties held August, 2006 in Boulder. The manuscript describing these results is in preparation for submission to the Journal of Chemical and Engineering Data

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